

# Sulfonated Poly(arylene ether ketone)s Prepared by Direct Copolymerization as Proton Exchange Membranes: Synthesis and Comparative Investigation on Transport Properties

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**ABSTRACT:** Sulfonated poly(aryl ether ketone)s (SPAEK) copolymers were synthesized by aromatic nucleophilic polycondensation from 3,3', 5,5'-tetramethyl-4, 4'-biphenol, 1,4-bis(4-fluorobenzoyl) benzene, and disulfonated difluorobenzophenone. The SPAEK membranes did not exhibit excessive swelling in hot water and at the same time show the proton conductivities in the range of 0.030 S/cm to 0.099 S/cm at 80°C. The methanol diffusion coefficients of the SPAEK membranes were in the range of  $4.7 \times 10^{-7}$  to  $8.1 \times 10^{-7}$  cm<sup>2</sup>/s measured at 25°C. The transport properties of this series of SPAEK copolymers were compared to poly(aryl ether ketone)s (SPEEK), poly(aryl ether ether ketone)s (SPEEKK), and Nafion<sup>®</sup> membranes. It was found that the transport properties (including proton conductivity and methanol permeability) follows the

trend of SPEEKK-60 < SPAEK-60 < SPEEK-60 < Nafion<sup>®</sup> 117, the order of which is also attributed to the differences in the chemical structure of the polymers and the membrane morphology. In general, this novel series of SPAEK membranes possess various advantages, such as low cost of the initial monomers, high thermal and mechanical stability, and low methanol permeability while simultaneously possessing sufficient proton conductivity, which makes them notably promising as proton exchange membrane (PEM) materials in direct methanol fuel cell (DMFC) applications. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 671–680, 2008

**Key words:** membranes; poly(ether ketones); polyelectrolytes; structure–property relations; swelling

## INTRODUCTION

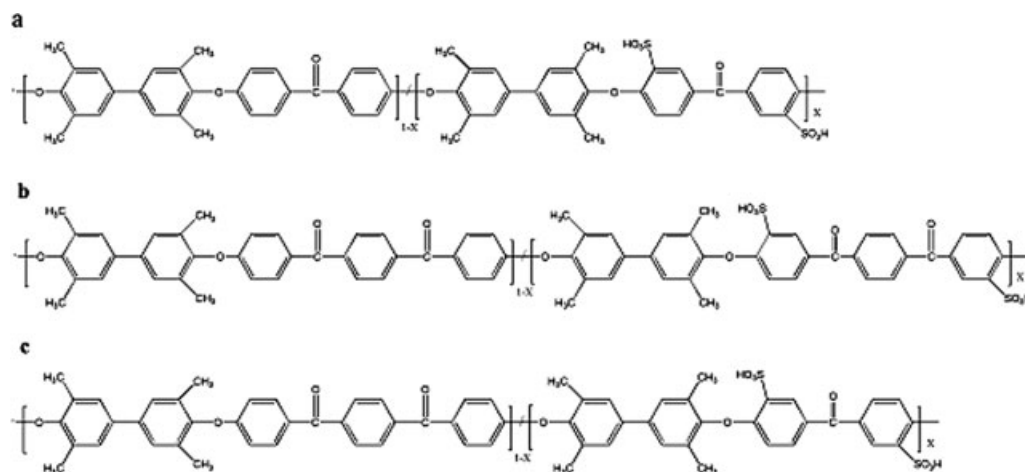
Proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) have been identified as environmentally attractive energy sources for applications in stationary power, automobiles, and portable electronics because of their low emissions and high conversion efficiency.<sup>1</sup> The proton exchange membrane (PEM), which is sandwiched between two platinum-porous catalytic electrodes, is regarded as a critical component of fuel cell system, serving as both electrolyte and separator.<sup>2</sup> Currently, the most commonly used membrane materials are perfluorinated sulfonic ionomers, such as Dupont Nafion<sup>®</sup>. These membranes exhibit excellent chemical and electrochemical stability in oxidizing environments as well as high proton conductivity when hydrated. However, their high cost, high methanol crossover, and loss of the preferable properties at high temperatures have limited their widespread commercial applica-

tions in PEMFC and other fuel cells.<sup>3</sup> Therefore, much effort has been stimulated in searching for alternative cost-effective PEM materials.

Among recently developed alternative proton conductive materials, sulfonated derivatives of high performance polymers, such as poly(arylene ether ketone)s,<sup>4,5</sup> polysulfone, poly(arylene ether sulfone),<sup>6,7</sup> polyimides,<sup>8</sup> and polybenzimidazole,<sup>9</sup> have attracted considerable attention because of their excellent chemical and mechanical stability, high thermo-oxidative stability, and low cost. Usually, they are prepared either by postsulfonation of the commercially available high performance polymer backbone or by direct copolymerization of sulfonated monomers.<sup>10,11</sup>

For the postsulfonation routine, the introduction of the sulfonate group is usually restricted to the activated position *ortho* to the aromatic ether bond, which may deteriorate the chemical and thermal stability of the polymer because of the cleavage of the ether linkage and elimination of the sulfonic acid groups from the activated aromatic ring via desulfonation. In addition, the degree of sulfonation ( $D_s$ ) is also hard to control, and too high a  $D_s$  value often

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**Scheme 1** Copolymer chemical structures synthesis in this work (a) SPEEK-XX; (b) SPEEKK-XX; (c) SPAEK-XX; (XX = 40, 50, 60).

results in the loss of membrane stability when immersing in hot water. Finally, the partial degradation and the side reactions might occur associated with postsulfonation reactions especially when power sulfonation agents such as chlorosulfonic acid are employed.<sup>12</sup> With respect to postsulfonation techniques, the direct polymerization of sulfonated monomers can easily and reproducibly place up to two sulfonic acid moieties per repeat unit on the deactivated ring positions, which might provide the resulting polymer architectures with the increased acidity, resulting in more facile proton transport.<sup>13</sup>

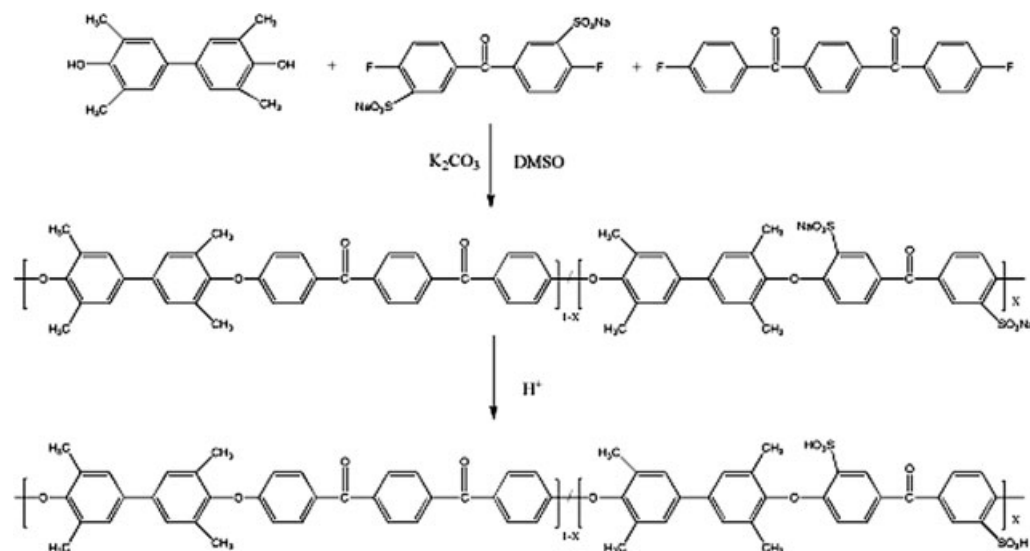
Recently many groups, including our own, have synthesized a series disulfonated poly(aryl ether ether ketone)s (SPEEKs) and disulfonated poly(aryl ether ether ketone ketone)s (SPEEKKs) by direct copolymerization of sulfonated monomers.<sup>14–16</sup> The transport properties of sulfonated copolymers are related to the states of aggregation of polymer chain segments, which is caused by the different structures of repeat units in polymer chains. In case of SPEEK polymer membrane, it shows sufficient proton conductivity at a high sulfonation level. Unfortunately, such a high sulfonation level results in the brittleness of the membranes at elevated temperatures and the relatively high methanol permeability, which poses a critical problem in reducing the practical application of a DMFC. Compared to SPEEK copolymers, the introduction of long and regular ether ether ketone ketone moieties in SPEEKK copolymers attributes to the increase of hydrophobicity and length of nonsulfonated segments and to make the hydrophilic segments well dispersed, thereby possibly resulting in the improvement of the mechanical properties of the membranes, hot water stability, and methanol resistance while simultaneous diminishment of proton conductivity.

To investigate the effect of the length of hydrophobic segments or hydrophilic segments on the properties related to the transport properties, a comparative series of sulfonated poly(aryl ether ketone)s (SPAEEK) copolymers were synthesized by aromatic nucleophilic polycondensation from 3,3', 5,5'-tetramethyl-4, 4'-biphenol, 1,4-bis(4-fluorobenzoyl) benzene, and 5,5'-carbonylbis(2-fluorobenzene-sulfonate) in this study. The transport properties of this series of SPAEEK copolymers were compared to SPEEK, SPEEKK copolymers. These three series of copolymers possess a similar chemical composition but different lengths of sulfonated or nonsulfonated segments. The chemical structures of these copolymers are shown in Scheme 1. The objective of this work is to investigate the relationship between the main-chain structure and transport to produce thermally and hydrolytically stable SPAEEK membranes with controlling proton conductivity and methanol permeability, which is important for liquid fed fuel cells.

## EXPERIMENTAL

### Copolymers synthesis and characterization

The series of SPEEK and SPEEKK copolymers were synthesized via aromatic nucleophilic substitution as described in our previous work in detail.<sup>14,15</sup> The copolymerization procedures for sulfonated poly(aryl ether ketone) copolymers were similar to those of SPEEKs, as shown in Scheme 2. Typical copolymerization for a 50% sulfonated copolymer was as follows. Sodium 5,5'-carbonylbis(2-fluorobenzene-sulfonate) (2.11 g, 5 mmol), 1,4-bis(4-fluorobenzoyl) benzene (1.61 g, 5 mmol), 3,3', 5,5'-tetramethyl-4, 4'-biphenol (2.42 g, 10 mmol), and potassium carbonate (1.587 g, 11.5 mmol) were charged to a three-neck



**Scheme 2** Synthesis of sulfonated poly(aryl ether ketone) copolymers (SPAEK-XX). SPAEK-40, SPAEK-50, SPAEK-60.

round-bottom flask equipped with a nitrogen inlet mechanical stirrer, a Dean-Stark trap, and a reflux condenser. After mixing the monomers in DMSO/toluene solvent system, the mixture was stirred at 140°C for 4 h and then raised to 180°C for 6 h. The reaction mixture was cooled to room temperature and poured into acetone. The inorganic salts were removed by washing with boiling water. The yields of all polymers were above 90 wt %. The resulting copolymer is referred to as SPAEK-XX, where XX represents the mol % of sulfonated repeat units, or the degree of sulfonation.

Inherent viscosities of the copolymers were measured in DMF at 25°C with a polymer concentration of 5.0 g/L. FTIR spectra of powder samples were recorded between 4000  $cm^{-1}$  and 400  $cm^{-1}$  on a Bruker Vector 22 FTIR spectrometer. The degree of sulfonation of the copolymers were estimated by  $^1H$  NMR (in  $d_6$ -DMSO) using a 500 MHz Bruker Avance 510 spectrometer. The chemical shift of tetramethylsilane was used as the internal reference standard.

Thermogravimetric analysis (TGA) was performed on a Pyris TGA (Perkin-Elmer) thermal analyzer. About 5–10 mg samples were kept at 150°C in the furnace for 20 min under  $N_2$  flow to remove any residual water or solvent remaining, then cooled to 80°C and then reheated to 700°C at a heating rate of 10°C/min.

### Membrane preparation

The salt form copolymers were first dissolved in DMF to afford transparent 10 wt % solutions, which were then cast onto clean glass plates. The glass plates were placed in a vacuum oven at 80°C for 6 h and at 120°C for another 12 h to remove the residual

solvent completely. Dry membranes were peeled off from the substrate with deionized water and converted to their  $H^+$  forms by immersing into 1.0M HCl solutions overnight. Finally, the membranes were stored in deionized water for 12 h to remove any excess HCl and dried under vacuum for 24 h.

### Transmission electron microscopy

Samples for transmission electronic microscopy (TEM) (JEM-2000EX) study were prepared by immersing the polymer powders in  $AgNO_3$  solution overnight to convert into their  $Ag^+$  form (SPAEEK-Ag). The SPAEEK-Ag polymers in DMF solutions were then cast onto copper grids before measurement.

### Membrane characterization

The mechanical properties of SPAEK membranes were evaluated on a SHIMADZU AG-I 1KN instrument using a strain rate of 2 mm/min at room temperature. The size of specimen is 15 mm  $\times$  4 mm, which was first dried at 80°C for 12 h and exposed for 1 h at  $\sim$  35% relative humidity.

The water uptake of the membrane was determined by measuring the change in the weight between the dry and swollen membranes. A detailed procedure was reported previously.<sup>16</sup> The ion exchange capacity (IEC) values were measured by a classical titration method. First, the membranes in the acid form ( $H^+$ ) were immersed into a 50 mL 1M NaCl solution for 24 h to completely exchange the  $H^+$  ions with  $Na^+$  ions. Then, the released  $H^+$  ions within the solutions were titrated with a 0.1M NaOH solution, using a phenolphthalein indicator.

The IEC values were recorded in unit of millimole NaOH per gram of the membrane samples (mequiv/g) as an average value for each sample.

Methanol diffusion coefficient was measured using a home-made glass diffusion cell, which consisted of two compartments and divided by a membrane sample. Hundred milliliter of pure methanol was placed on one side of the diffusion cell (cell A) and 100 mL water was placed on the other side (cell B). Both compartments were continuously stirred using submersible magnetic stirrers. The concentration of the methanol in cell B was measured by using SHIMADZU GC-8A chromatograph. Peaks areas were converted to the methanol concentration with a calibration curve. The methanol diffusion coefficient was calculated by the reference report.<sup>16</sup>

The proton conductivities of the membranes were measured by AC impedance spectroscopy over a frequency range of 10–10<sup>7</sup> Hz with voltage 50–500 mV, using an impedance/gain-phase analyzer (Solatron 1260, Solatron Analytical, UK) in combination with an electrochemical interface (Solatron 1287). Conductivity measurement of fully hydrated membranes was carried out with the cell immersed in liquid water. The proton conductivity was calculated by formula (1):

$$\sigma = L/RA \quad (1)$$

where  $\sigma$  is proton conductivity in S/cm,  $L$  the distance between the two electrodes, and  $A$  the cross-sectional area of membrane.  $R$  is derived from the low intersection of the high frequency semicircle with the Re ( $Z$ ) axis on a complex impedance plane.

## RESULTS AND DISCUSSION

### Syntheses and characterization of SPAEKs copolymers

As shown in Scheme 2, the SPAEKs were synthesized by a nucleophilic aromatic substitution (S<sub>N</sub>Ar) polycondensation of activated aromatic halides with 3,3', 5,5'-tetramethyl-4, 4'-biphenol under standard conditions. The polymerization compositions and some properties of these copolymers are summarized in Table I. The intrinsic viscosity of the copolymers was above 0.7 dL/g in DMF at 25°C, indicating that high molecular weights were obtained. This result was also evidenced by the fact that they could be cast into tough, ductile membranes from their DMF solutions.

<sup>1</sup>H NMR spectroscopy provided unambiguous structure elucidation and was also used to quantify the experimental  $D_s$ , which is defined as the average number of sulfonic groups per repeating unit of the synthesized copolymers.<sup>17,18</sup> The aromatic regions of

**TABLE I**  
The Polymerization Results and Analytical Data

Polymer	Percentage of sulfonated monomer (mol %)	$D_s$ (c) <sup>a</sup>	$D_s$ (m) <sup>b</sup>	Yield (%)	$\eta_{sp}/c$ <sup>c</sup>
SPAEEK-40	40	0.8	0.72	95	0.71
SPAEEK-50	50	1.0	0.84	94	0.87
SPAEEK-60	60	1.2	1.22	94	0.83
SPEEK-60 <sup>d</sup>	60	1.2	1.10	93	0.94
SPEEKK-60 <sup>e</sup>	60	1.2	1.23	93	1.41

<sup>a</sup> Degree of sulfonation calculated from the percentage of sulfonated monomer.

<sup>b</sup> Degree of sulfonation measured experimentally by <sup>1</sup>H NMR.

<sup>c</sup>  $\eta_{sp}/c$  was measured at a concentration of 0.5 g/dL in DMF at 25°C.

<sup>d</sup> Data adapted from Ref. 14.

<sup>e</sup> Data adapted from Ref. 15.

<sup>1</sup>H NMR spectra of SPAEK copolymers dissolved in DMSO-*d*<sub>6</sub> are shown in Figure 1. A sharp peak is observed at about 8.15–8.36 ppm due to the aromatic protons adjacent to the sulfonic group (H<sub>1</sub>). Therefore, the  $D_s$  can be measured by comparing the intensity of this signal H<sub>1</sub> with the intensities of the remaining aromatic signals. The  $D_s$  is obtained from the integration ratio of these signals according to the following eq. (2).

$$\frac{i_1}{i_R} = \frac{D_s}{16 - 4D_s} \quad (2)$$

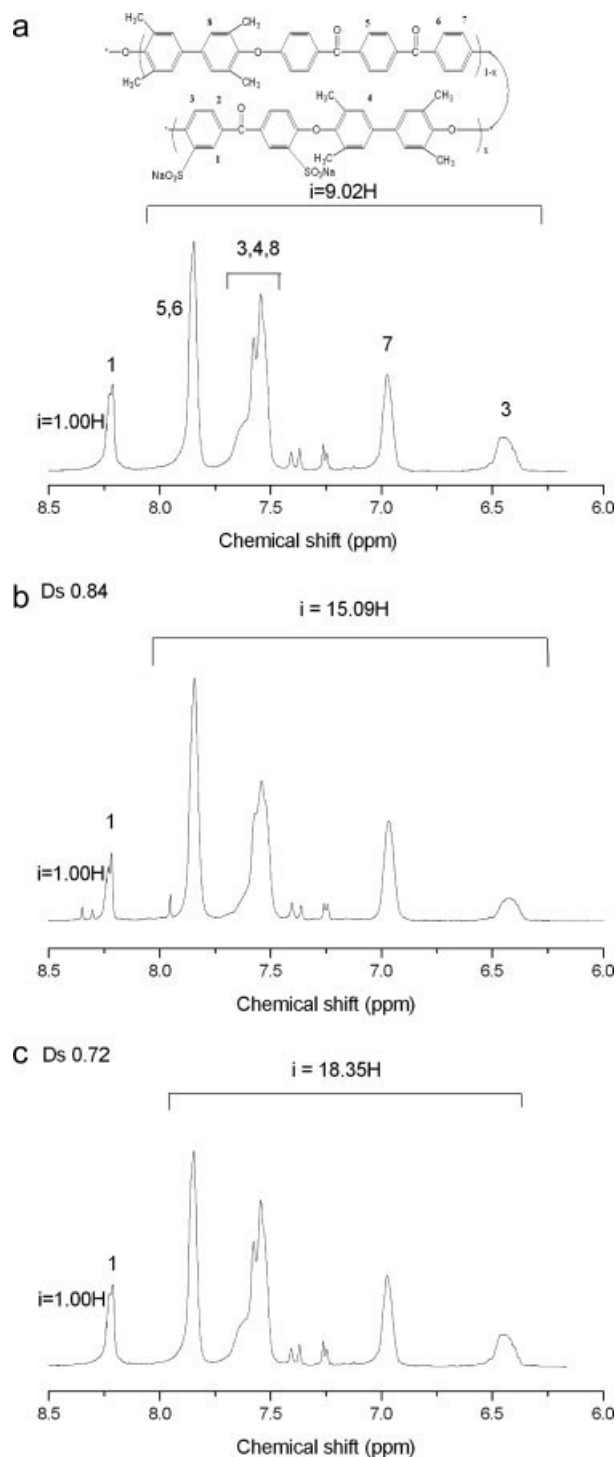
Equation (2) can be expressed as

$$D_s = \frac{16i_1}{i_R + 4i_1} \quad (3)$$

where  $i_1$  is the intensity of H<sub>1</sub> (8.2 ppm),  $i_R$  is the intensity of the remaining aromatic signals (6.33–7.91 ppm).

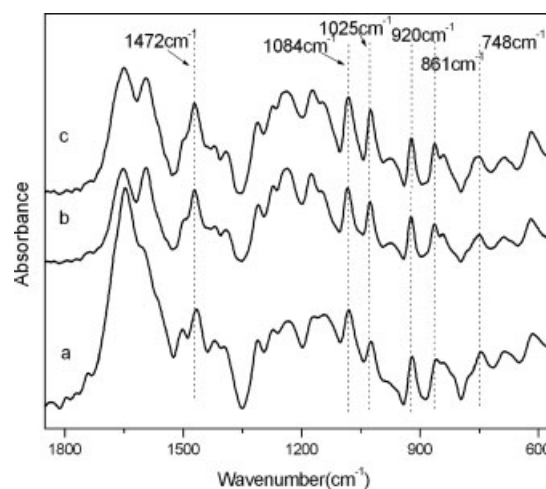
Here, SPAEK 60 was taken as an example to illustrate the  $D_s$  measurement technique. The signal of intensity value of sulfonated repeating unit protons H<sub>1</sub> was first set to 1.00H, and the resulting total signal intensity for the remaining aromatic signals was 9.02H, hence, a calculated  $D_s$  value of 1.22. This result is in good agreement with the one expected from the copolymer composition. This indicated that  $D_s$  could be readily controlled by varying the feed ratios of sulfonated monomers to nonsulfonated monomers.

Successful introduction of the sodium sulfonate groups into PAEK copolymers was confirmed by Fourier transform infrared (FTIR) spectroscopy (Fig. 2). The absorption bands at round 748, 861, and



**Figure 1**  $^1\text{H}$  NMR spectrum of SPAEK copolymers with various  $D_s$  (a) SPAEK-60 with  $D_s$  1.22; (b) SPAEK-50 with  $D_s$  0.84; and (c) SPAEK-40 with  $D_s$  0.72.

$920\text{ cm}^{-1}$  correspond to tetra-substitution on aromatic phenyl for SPAEK copolymers. The out of plane around  $920\text{ cm}^{-1}$  is taken as a standard within the experimental error range to compare the intensities for characteristic bands. Absorption bands around  $1025$  and  $1084\text{ cm}^{-1}$  can be assigned to



**Figure 2** FTIR spectra of SPAEK-40 (a), SPAEK-50 (b), and SPAEK-60 (c) copolymers in sodium form.

symmetric and asymmetric stretching vibrations of sodium sulfonate groups. The characteristic band around  $1472\text{ cm}^{-1}$  arises from trisubstitution of benzene rings caused by the introduction of sodium sulfonate groups, and that around  $1652\text{ cm}^{-1}$  is due to aryl carbonyl groups. The intensity of the  $1025$ ,  $1084$ , and  $1472\text{ cm}^{-1}$  bands increase obviously with increasing  $D_s$ .

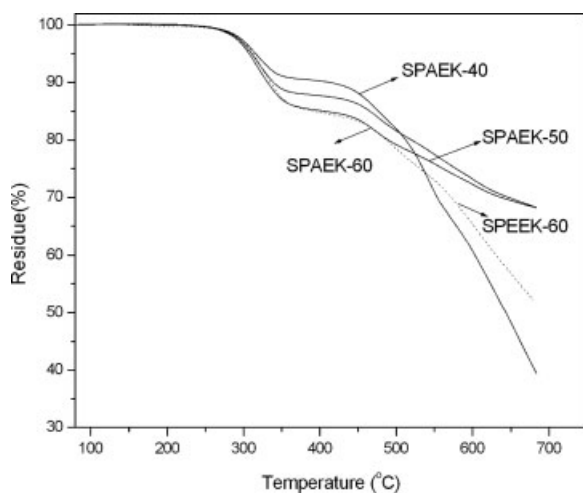
The thermal stabilities of the SPAEK copolymers were investigated by under  $\text{N}_2$  atmosphere at a heat rate of  $10^\circ\text{C}/\text{min}$ . The onset temperatures for decomposition steps are given in Table II, and the thermograms are shown in Figure 3. In similarity with SPEEK-60, SPAEK copolymers in the acid form exhibit two distinct thermal degradation steps. The first weight loss step at about  $280^\circ\text{C}$ , which is believed to be associated with the splitting-off of sulfonic acid groups and the second weight loss step starting at about  $450^\circ\text{C}$ , which corresponds to the main polymer chain of decomposition.<sup>19</sup> The 5 wt % weight loss temperatures of SPAEK-40 to SPAEK-60 are, respectively,  $316$ ,  $310$ , and  $307^\circ\text{C}$  and show a decreasing tendency with the increase of  $D_s$ . This may be explained by the relatively lower degrade temperatures for sulfonated groups than polymer backbone.<sup>15</sup> In addition, the degradation rate of the

**TABLE II**  
TGA Results of SPAEK Copolymers

Polymer	$T_{d5\%}$ ( $^\circ\text{C}$ ) <sup>a</sup>	$T_d$ ( $^\circ\text{C}$ ) <sup>b</sup>	
		The first stage	The second stage
SPAEEK-40	316	282	482
SPAEEK-50	310	280	453
SPAEEK-60	307	280	452
SPEEK-60	313	289	454

<sup>a</sup> 5% weight loss temperature measured by TGA.

<sup>b</sup> Onset temperature of decomposition.



**Figure 3** TGA curves of SPAEK copolymers under nitrogen.

polymer backbone for SPAEK-40 is higher than the other two samples at the temperature above 500°C. It can be explained by the much lower molecular weight ( $\eta_{sp}/c$  0.71) than the others ( $\eta_{sp}/c \geq 0.83$ ). Generally, all the polymers show excellent thermal stability, which indicates that they are adequate for application in PEMFC.

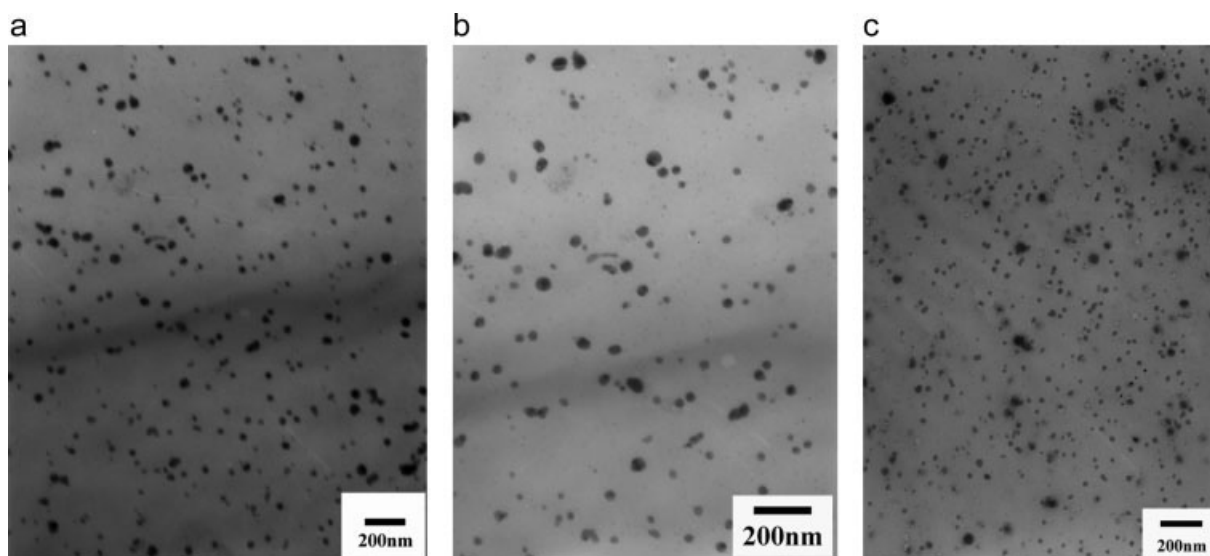
### Microstructure of membranes

The morphology of SPAEK membranes is expected to play an important role in determining their physical and electrochemical behaviors, such as proton conductivity, water uptake, and mechanical strength.<sup>20–22</sup> Eisenberg reported that sulfonated groups could aggregate into hydrophilic clusters, which can pro-

vide cation transport pathway or ionic transport channels.<sup>23</sup> To investigate phase separation and ionic aggregations, TEM analysis was performed on the membranes stained with silver ions.<sup>20,24</sup> TEM images for the SPAEK membranes possessing different degrees of sulfonation are shown in Figure 4. The dark areas are assigned to localized domains of  $-\text{SO}_3\text{Ag}$  and the brighter areas represent the hydrophobic domain (polymer backbone). As is clearly seen in the images, silver particles disperse within the SPAEK matrix randomly. The similar microstructure has been reported for the other series of SPEEK or SPEEKK copolymers.<sup>14,15</sup> With an increment in the degree of sulfonation from SPAEK-40 to SPAEK-60 membrane, the density of sulfonic groups increases, resulting in the formation of higher density of silver particles within SPAEK matrix. Therefore, it is concluded that the ionic groups could aggregate to relatively large domains at high ion contents.<sup>25</sup> This may be likely to promote proton transport properties of SPAEK membranes.

### Mechanical properties

It is essential for PEMs to possess adequate mechanical strength to withstand fabrication of the membrane electrode assembly. Here, the tensile test of membranes was conducted at ambient conditions with  $\sim 35\%$  relative humidity, and the results are summarized in Table III. For comparison, SPEEK-60 and SPEEKK-60 were also tested under the same conditions. The initial Young's modulus for the membranes of SPAEK-40, -50, and -60 are 2.09, 1.51, and 1.75 GPa, respectively, which are higher than the ones of SPEEK-60 (1.01 GPa), SPEEKK-60 (1.70



**Figure 4** TEM micrograph of SPAEK membranes (a) SPAEK-40; (b) SPAEK-50; and (c) SPAEK-60.

**TABLE III**  
The Mechanical Properties of the Membranes

Polymer	Tensile strength (Mpa)	Maximum elongation (%)	Tensile modulus (Gpa)
SPAEK-40	71.01	22.50	2.09
SPAEK-50	51.24	13.18	1.51
SPAEK-60	62.79	19.64	1.75
SPEEK-60	49.14	22.76	1.01
SPEEKK-60	49.99	8.07	1.70

GPa), and Nafion 117. All the three membranes exhibit the elongation at break of 22, 13, and 19%, and tensile strength ranging from 51 to 71 MPa. These data are comparable to those of other series of sulfonated poly(arylene ether ketone)s membranes, indicating that SPAEK-XX copolymers showed better mechanical stability than SPEEK and SPEEKK based ones. As expected, due to the increment in the hydrophobicity of the polymer backbone, the hydrophilic segments could disperse well in the SPAEK copolymers matrix. Therefore, the mechanical properties of SPAEK membranes could be improved.

It should be noted that the mechanical properties of the SPAEK-XX samples do not have the same tendency with increasing  $D_s$ . Various factors could influence the mechanical properties of membranes including: the characteristic of polymers such as molecular weight, the chemical composition, the intermolecular dissociation of the sulfonate moieties, etc., and the characteristic of membranes such as the structure, the solvents used during membranes casting, the uniformity of membrane, etc. So, the content of sulfonate groups has no obvious effect on the mechanical properties of membranes from the results. The similar phenomenon was also detected from the results of SPEEK series copolymers.<sup>26</sup>

### Ion exchange capacity and water uptake

It has been widely reported in the literatures that the proton conductivity of sulfonated polymers is

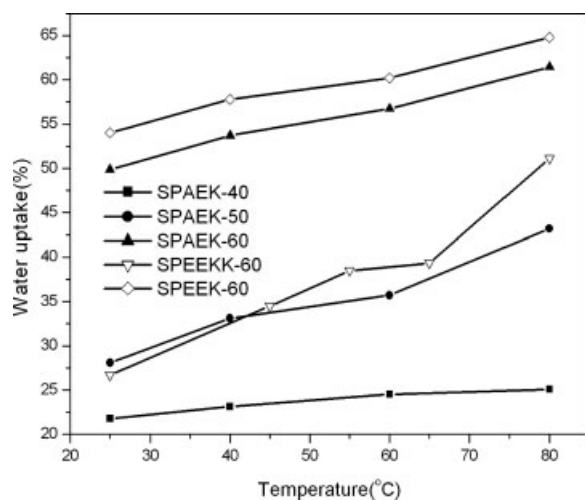
known to be associated with the IEC and water uptake of the membranes.<sup>27</sup> Generally, proton conductivity depends on the density of available sulfonic acid groups and their dissociation capability in water. Water molecules attach to the acid functionality and facilitate proton transport. However, excessively high levels of water uptake result in membrane swelling, mechanical fragility, low dimension stability, and high methanol permeability. Therefore, the preparation of sulfonated polymers with ideal water uptakes and dimensional stability are important for creating new membrane materials for fuel cell system.

IEC and water uptake values are shown in Table IV. To ascertain structure–property relationships, SPAEK-60 polymer was compared to other two series of sulfonated poly(arylene ether ketone)s such as SPEEK-60 and SPEEKK-60, whose structures are presented in Scheme 1. SPEEK-60 membrane was used as a reference experiment PEM because it has the same hydrophilic unit but different length of the hydrophobic unit, while SPEEKK-60 represented an example of the same hydrophobic unit but different hydrophilic unit. As expected, these SPAEK membranes showed an increased tendency in IEC and water uptake with the increasing degrees of sulfonation, which are due to the strong hydrophilicity of the sulfonic acid groups. For example, SPAEK membranes with degrees of sulfonation of 0.72, 0.84, and 1.22 exhibited water uptake values at 25°C of 22, 28, and 50%, respectively. Otherwise the IEC values increased from 0.96 to 1.66 mequiv/g. At similar percentage of sulfonated monomer (60%) for polymer syntheses, the SPAEK-60 membrane showed slightly lower water uptake value than that of SPEEK-60 membrane, while it showed higher than the SPEEKK-60 membrane. This can be attributed to the nature of the polymer backbone, the content of sulfonic acid groups, and how the water is bound within its microstructure.<sup>28</sup> The increase in the molecular weight of the repeating unit effectively reduces the amount of ionic groups in a unit weight of the polymer thus reducing the IEC and water

**TABLE IV**  
The Analytical Parameters of SPAEK Membranes

Samples	IEC (mequiv/g)	Methanol permeability (cm <sup>2</sup> /s)	Water uptake (%)		Proton conductivity (S/cm)	
			25°C	80°C	25°C	80°C
SPAEK-40	0.96	$4.7 \times 10^{-7}$	22	25	0.013	0.030
SPAEK-50	1.35	$5.9 \times 10^{-7}$	28	43	0.025	0.054
SPAEK-60	1.66	$8.1 \times 10^{-7}$	50	61	0.048	0.099
SPEEK-60	1.92	$1.74 \times 10^{-6}$	54	65	0.070	0.134
SPEEKK-60	1.57	$6.6 \times 10^{-7}$	27	48	0.047	0.063
Nafion <sup>®</sup> 117 <sup>a</sup>	0.92	$2.38 \times 10^{-6}$	38	–	0.077	0.129

<sup>a</sup> Data adapted from Refs. 14 and 15.



**Figure 5** Water uptake of SPAEK membranes at different temperatures.

uptake values. Second, due to the increase in the hydrophobicity of the polymer backbone, the water repellency of the polymer increases leading to water uptake values decreasing.

Since PEMs in fuel cells are generally operated at temperatures close to 80°C, water uptake of these membranes were measured as functions of temperature.<sup>29</sup> The results are shown in Figure 5. The water uptake of membranes at 80°C showed the similar tendency as function of IEC. The shapes of the water uptake versus temperature curves for all the membranes were found to be similar. The water uptake values increased sharply with temperature. This can be explained that the polymer chain mobility and the free volume for water absorption increase at elevated temperatures. It is noteworthy that all the membranes maintained their dimensional stability at 80°C. This suggests that they could meet the demands for operation at elevated temperatures as PEMs.

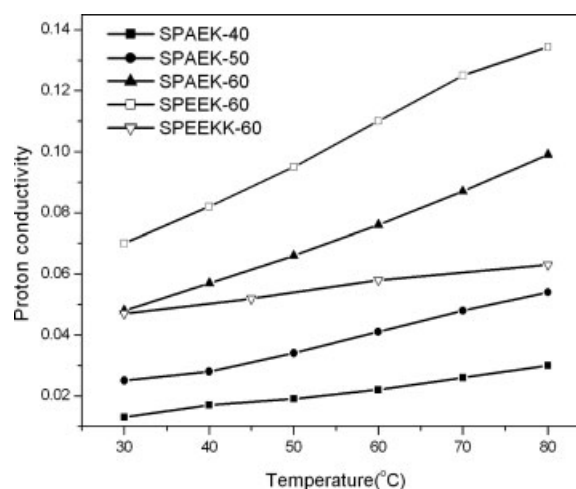
### Proton conductivity and methanol permeability

The proton conductivities of the membranes possessing different degrees of sulfonation were estimated by ac impedance spectroscopy. The conductivity data are listed in Table IV and plotted in Figure 6 as a function of temperature. The conductivity of SPEEK-60 and SPEEKK-60 were included for comparison. As expected, increasing IEC increased the conductivity of the SPAEK membranes, because conductivity depended on the concentration density of the ionic groups. For example, SPAEK membranes with IEC of 0.96, 1.35, 1.66 mequiv/g exhibited conductivities at 25°C of 0.013, 0.025, and 0.048 S/cm, respectively. In common with the results found in

many others studies, the conductivity of SPAEK membranes increased with temperature.<sup>5,6</sup> The conductivity of SPAEK-60 increased to 0.099 S/cm at 80°C, which is considered high enough for PEM operation in fuel cell system.

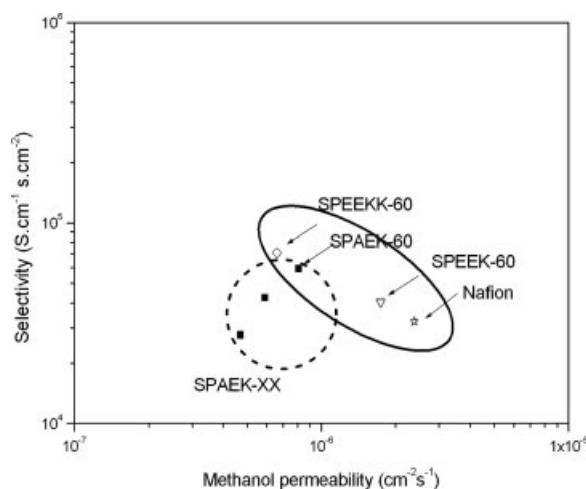
In comparison with SPEEK-60 membrane, SPAEK-60 with the same 60% mole percent of the disulfonation units had lower proton conductivity values. However, it exhibited higher proton conductivity values than those of SPEEKK-60 membrane, especially at 80°C. It is also noted that the increment of conductivity versus temperature is not in the same magnitude, seen from the slope of these membranes shown in Figure 6. It is well known that the properties of the PEM are strongly dependent on the chemical structure of the copolymers as well as morphology. The extreme hydrophobicity of the polymer backbone and extreme hydrophilicity of the sulfonic acid groups lead to a spontaneous hydrophilic/hydrophobic nano-separation.<sup>30</sup> This separation structure of these materials plays an important role in protonic, water, and methanol transport. Compared to SPEEKK with the same degree of sulfonation, SPEEK show much more interconnected ion clusters and more clearly phase separated. This may be explained that the distance between sulfonate groups in SPEEK is relatively shorter than that in SPEEKK, which is benefit for the sulfonic acid groups to form clusters and undergo a certain level of self-assembly.

One of the major drawbacks of the commercial Nafion<sup>®</sup> membrane as a PEM in DMFC systems is its high methanol permeability. In comparison to Nafion<sup>®</sup> 117, SPAEK membranes show much lower methanol diffusion, which are in the range of  $4.7 \times 10^{-7}$  to  $8.1 \times 10^{-7}$  cm<sup>2</sup>/s measured at 25°C. As reported previously, the methanol permeability



**Figure 6** Proton conductivities of SPAEK membranes at different temperatures.





**Figure 7** Selectivity ( $\Phi$ ) of SPAEK-XX, SPEEK-60, SPEEKK-60, and Nafion 117 membranes.

increases with an increase in IEC.<sup>5,6</sup> Similar to proton conductivity, the methanol permeability follows the trend of SPEEKK-60 < SPAEK-60 < SPEEK-60 < Nafion<sup>®</sup> 117, the order of which is attributed to the different membrane morphology. It appears that both proton conduction and methanol permeation occur through the same pathway or ionic channels formed by the interconnected hydrophilic domains in the membrane. These interconnected hydrophilic domains strongly contribute to high proton conductivity, but at the same time they may promote high methanol diffusion.<sup>31</sup>

There is a strong tradeoff relationship between the proton conductivity and the methanol permeability when designing a new PEM for DMFC applications.<sup>32</sup> Figure 7 shows the selectivity ( $\Phi$ ) to methanol permeability of the SPAEK-XX, SPEEK-60, SPEEKK-60, and Nafion 117 membranes.<sup>33</sup> Here, the selectivity is defined by the ratio of proton conductivity to methanol permeability measured at room temperature, which is a characteristic factor for evaluating membrane performances. Seen from the Figure 7, SPAEK-60 and SPEEKK-60 show a relatively higher selectivity, than that of Nafion 117 and SPEEK membranes, which is attractive in DMFC.<sup>34</sup>

## CONCLUSIONS

A series of novel SPAEK copolymers were synthesized by aromatic nucleophilic copolycondensation of the 3,3', 5,5'-tetramethyl-4, 4'-biphenol with various amounts of 1,4-bis(4-fluorobenzoyl) benzene and sodium 5,5'-carbonylbis(2-fluorobenzene-sulfonate). The obtained membranes exhibited good thermal and mechanical properties. Selected properties of this series of SPAEK copolymers were compared to

SPEEK, SPEEKK copolymers obtained by our groups previously. These three series of copolymers possess a similar chemical composition but different chain lengths of sulfonated or nonsulfonated unit. The SPAEK membranes did not exhibit excessive swelling in hot water and at the same time show the proton conductivities in the range of 0.030–0.099 S/cm at 80°C. It was found that the transport in the SPAEK membrane was much higher than that in the SPEEKK for a given  $D_s$ , while lower than that in the SPEEK. The methanol diffusion coefficients of the SPAEK membranes were in the range of  $4.7 \times 10^{-7}$  to  $8.1 \times 10^{-7}$  cm<sup>2</sup>/s measured at 25°C. Similar to proton conductivity, the methanol permeability follows the trend of SPEEKK-60 < SPAEK-60 < SPEEK-60 < Nafion<sup>®</sup> 117, the order of which is also attributed to the difference in chemical structure of the polymers and membrane morphology. Consequently, this novel series of SPAEK membranes show improvement in mechanical properties, low cost of the initial monomers, high thermal stability, and low methanol permeability while simultaneously possessing sufficient proton conductivity, making SPAEK membranes as notably promising as PEM materials in DMFC applications.

## References

- Murray, E. P.; Tsai, T.; Barnett, S. A. *Nature* 1999, 400, 649.
- Rikukawa, M.; Sanui, K. *Prog Polym Sci* 2000, 25, 1463.
- Kerres, J. J. *J Membr Sci* 2001, 185, 3.
- Xing, P. X.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Kaliaguine, S. *Macromolecules* 2004, 37, 7960.
- Kaliaguine, S.; Mikhailenko, S. D.; Wang, K. P.; Xing, P.; Robertson, G.; Guiver, M. D. *Catal Today* 2003, 82, 213.
- Wang, F.; Hickner, M. A.; Kim, Y. S.; Zawodzinski, T. A.; McGrath, J. E. *J Membr Sci* 2002, 197, 231.
- Harrison, W. L.; Hicker, M. A.; Kim, Y. S.; McGrath, J. E. *Fuel Cells* 2005, 5, 201.
- Genies, C.; Mercier, R.; Sillion, B.; Cornet, N.; Gebel, G.; Pineri, M. *Polymer* 2001, 42, 359.
- Ma, Y. L.; Wainright, J. S.; Litt, M. H.; Savinell, R. F. *J Electrochem Soc* 2004, 151, A8.
- Genova-Dimitrova, P.; Baradie, B.; Foscallo, D.; Poinson, C.; Sanchez, J. Y. *J Membr Sci* 2001, 185, 59.
- Wang, F.; Chen, T. L.; Xu, J. P. *Macromol Chem Phys* 1998, 199, 1421.
- Trotta, F.; Drioli, E.; Moraglio, G.; Poma, E. B. *J Appl Polym Sci* 1998, 70, 477.
- Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem Rev* 2004, 104, 4587.
- Gil, M.; Ji, X. L.; Li, X. F.; Na, H.; Hampsey, J. E.; Lu, Y. F. *J Membr Sci* 2004, 234, 75.
- Li, X. F.; Liu, C. P.; Lu, H.; Zhao, C. J.; Wang, Z.; Xing, W.; Na, H. *J Membr Sci* 2005, 255, 149.
- Li, X. F.; Zhao, C. J.; Lu, H.; Wang, Z.; Na, H. *Polymer* 2005, 46, 5820.
- Gao, Y.; Robertson, G. P.; Guiver, M. D.; Jian, X. *J Polym Sci Part A: Polym Chem* 2003, 41, 497.
- Shi, Z. Q.; Holdcroft, S. *Macromolecules* 2005, 38, 4193.
- Zaidi, S. M. J.; Mikhailenko, S. D.; Robertson, G. P.; Guiver, M. D.; Kaliaguine, S. *J Membr Sci* 2000, 173, 17.

20. Yang, Y. S.; Shi, Z. Q.; Holdcroft, S. *Macromolecules* 2004, 37, 1678.
21. Ding, J. F.; Chuy, C.; Holdcroft, S.; *Adv Funct Mater* 2002, 12, 389.
22. Won, J.; Park, H. H.; Kim, Y. J.; Choi, S. W.; Ha, H. Y.; Ha, I.-H. *Macromolecules* 2003, 36, 3228.
23. Eisenberg, A. *Macromolecules* 1970, 3, 147.
24. Yin, Y.; Fang, J. H.; Watari, T.; Tanaka, K. *J Mater Chem* 2004, 14, 1062.
25. Williams, C. E.; Russell, T. P.; Jerome, R.; Horrion, J. *Macromolecules* 1986, 19, 2877.
26. Li, X. F.; Wang, Z.; Lu, H.; Zhao, C. J.; Na, H.; Zhao, C. *J Membr Sci* 2005, 254, 147.
27. Xing, P. X.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Wang, K. P.; Kaliaguine, S. *J Membr Sci* 2004, 229, 95.
28. Fujimoto, Cy. H.; Hickner, M. A.; Cornelius, C. J.; Loy, D. A. *Macromolecules* 2005, 38, 5010.
29. Xing, P. X.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Kaliaguine, S. *Polymer* 2005, 46, 3257.
30. Bai, Z.; Durstock, M. F.; Dang, T. D. *J Membr Sci* 2006, 281, 508.
31. Hickner, M. A.; Fujimoto, Cy. H.; Cornelius, C. J. *Polymer* 2006, 47, 4238.
32. Roy, A.; Hickner, M. A.; Yu, X.; Li, Y.; Glass, T. E.; McGrath, J. E. *J Polym Sci Part B: Polym Phys* 2006, 44, 2226.
33. Kang, M.-S.; Kim, J. H.; Won, J.; Moon, S.-H.; Kang, Y. S. *J Membr Sci* 2005, 247, 127.
34. Xue, S.; Yin, G. *Polymer* 2006, 47, 5044.